Eu-induced lattice vibrations in Gd_2O_3 crystals

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Eu-induced lattice vibrations in Gd_2O_3 crystals

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Abstract. The effect of trivalent Eu impurity occupying a position with the S_6 site symmetry in cubic Gd_2O_3 on the latter's structure and phonon spectrum is investigated. This study was performed by means of computer modeling within a shell model. The equilibrium structures and phonon local symmetrized densities of states were calculated. In addition, frequencies of localized vibrations induced by Eu ion were determined. The calculated results were compared with the available experimental data in literature.

1. Introduction

Gadolinium oxide (Gd_2O_3) is one of the representatives of a group that consists of 17 sesquioxides of rare earths with different atomic numbers. Gadolinium sesquioxide is a material with wide technological applications ranging from magnetic to optoelectronic and nuclear fields [1]. It can be used in monocrystalline or powder and nanosized states as well as in thin-film form. A structural phase diagram for the lanthanide sesquioxides shows that at temperatures below approximately 1200°C single Gd_2O_3 crystal exists in a cubic C-type phase. This crystalline phase has the bixbyite structure with space group Ia-3. In the following, we will consider only cubic Gd_2O_3.

Physical properties of defect-free gadolinium oxide such as structural [2–8], electronic [6–8], vibrational [9–12], thermodynamical [13] have been thoroughly studied both experimentally and theoretically. Additionally, various properties of Gd_2O_3 doped with rare earth elements have been studied too, for example in [14–16]. It is worth noting that rare earth-doped Gd_2O_3 crystals are promising systems that are used in solid-state lasers, display devices, etc.

Over the last few decades, interest in europium-doped Gd_2O_3 has grown considerably due to specific photoluminescence properties [17–20]. Less attention has been paid to the study of the lattice strain and vibrational properties of Gd_2O_3 doped with europium (Eu^{+3}). Meanwhile, a comprehensive description of the dynamic processes in Gd_2O_3-based materials is impossible without knowledge about localized vibrations caused by defects. The microscopic mechanisms of the processes taking place are still not fully understood. In the present paper, we focus on the investigation of local atomic structures and defect vibrations of Gd_2O_3 with trivalent Eu substitutional impurities which occupy Wyckoff 8b positions with the S_6 symmetry.

2. Computational Procedures

The lattice structure of Gd_2O_3 containing Eu impurities and frequencies of localized vibrations due to these impurities were calculated within the framework of a cluster approach [21]. The crystal is

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divided into an inner spherical region containing the defect and an outer region with the remaining ions. The inner region is large enough. In this region interactions between atoms are considered at a microscopic level. Outer region is treated in the approximation of a polarizable continuum and extends to infinity.

To describe the interatomic interactions we used the realistic shell model [22]. This ionic model takes into account the long-range Coulomb interaction between cores and the interaction between shells, the potential of which consists of two parts: the Coulomb term and the short-range term. The short-range potential used here is the Buckingham potential with parameters proposed by Lewis [23]. It was shown that, with the this potential, the calculated lattice constant of 10.721 Å, bulk modulus of 161.7 GPa and heat capacity of 101.0 J K^{-1} mol^{-1} for perfect gadolinium oxide are in good agreement with the experimental data of 10.817 Å [4], 117.6 GPa [24] and 105.5 J K^{-1} mol^{-1}[13], respectively.

The structure optimization of Gd_2O_3:Eu was performed through minimizing the lattice energy. For this we have employed the lattice static method [25]. The local energy minimum was achieved iteratively using the Newton–Raphson matrix method. The inverse matrix of second derivatives of the energy was updated at each iteration based upon BFGS method.

An analysis of local symmetrized densities of states (LSDOS) of phonons in perfect Gd_2O_3 and defective Gd_2O_3:Eu made it possible to estimate the effect of Eu^{+3} ions on the vibrational spectrum and to define the frequencies of localized vibrations. The method, which has been used for the calculation of these LSDOS, is the recursion method [26], which is rather efficient. The first step of the recursion method is to select the initial vector of the vibrational state of an appropriate symmetry. The projection operator method was applied to determine the symmetry coordinates of this starting vector.

3. Results and Discussion

3.1. Local atomic structure

First, we consider the lattice structure of perfect Gd_2O_3 crystals. Our calculations show that Gd1 ion located at the S_6 site is bonded to six O ions at 2.312 Å. These oxygens form first coordination shell (see figure 1). Six nearest Gd2 ions located at C_2 sites form second coordination shell at a distance of 3.576 Å. These data are close to those obtained earlier the extended X-ray absorption fine structure method [7].

In Eu-doped Gd_2O_3, the distances between Eu^{+3} ion and nearest ions are found to be greater than bond lengths in the defect-free crystal. The calculated results of distances between some ions are listed in Table 1. Unfortunately, the authors do not know experimental data on the structure of cubic Gd_2O_3 when Gd^{+3} ions are replaced by Eu^{+3} ions. However, the obtained values are in good agreement with the fact that the Gd^{+3} ionic radius (0.94 Å) is slightly less than Eu^{+3} ion (0.95 Å).

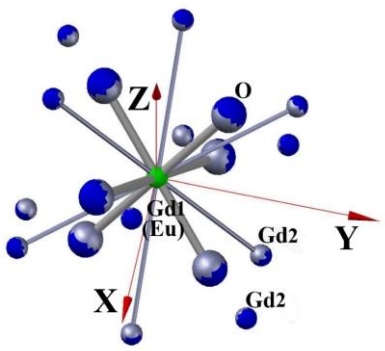

Figure 1. The local configurations around Gd^{+3} ion on the S_6 site in Gd_2O_3 (grey spheres) and around Eu^{+3} impurity in Gd_2O_3:Eu (blue spheres).

Table 1. Interionic distances (Å) for Gd_2O_3 and Gd_2O_3:Eu^{+3}.

Ions	Coordination number	Gd_2O_3		Gd_2O_3:Eu^{+3}
		This work	Expt.[7]	This work
Gd1[or Eu]–O	6	2.312	2.308	2.320
Gd1[or Eu]–Gd2	6	3.576	3.570	3.580
Gd1[or Eu]–Gd2	6	4.017		4.019

3.2. Vibrational Dynamics for Gd_2O_3:Eu

Since Gd^{+3} and Eu^{+3} ions in Gd_2O_3 and Gd_2O_3:Eu crystals is surrounded by six O^{-2} ions as nearest neighbors, the phonon LSDOS projected onto ion vibrational displacements of GdO_6 and EuO_6 units have been calculated. O^{-2} ions participate in the vibrations of the A_g-, A_u-, E_g- and E_u-symmetries. Vibrational symmetry modes in which the motion of Gd^{+3} and Eu^{+3} ions is involved are under the representations of A_u and E_u.

For example, figure 2 shows the phonon LSDOS projected onto A_u-symmetry displacements of Gd1 ion and O ions in Gd_2O_3 and Eu ion and O ions in Gd_2O_3:Eu. According to our calculations Gd^{+3} and Eu^{+3} ion motions dominate up to 7 THz. Oxygen movement plays a great role at the high frequencies above 8 THz. When Eu impurity is created, the low-frequency band of the phonon density is shifted to the low-frequency part of the spectrum. The frequencies of localized symmetrized vibrations induced by Eu impurity are summarized in Table 2.

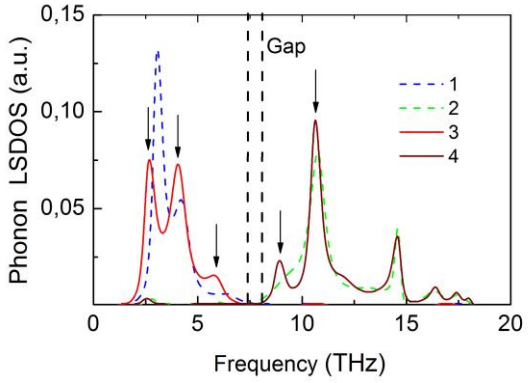

Figure 2. Phonon LSDOS projected onto A_u-symmetry displacements of Gd1 ion (curve 1), O ions (curve 2) in Gd_2O_3 and Eu ion (curve 3), O ions (curve 4) in Gd_2O_3:Eu. The arrows indicate to the localized vibrations.

Table 2. Frequencies (THz) of localized vibrations in Gd_2O_3 with Eu^{+3} on the position 8b.

Ions	Mode	Vibration symmetry			
		A_g	A_u	E_g	E_u
Eu			2.6, 4.2, 6.2		2.6, 4.4, 6.6
O	stretching	10.8, 16.8, 17.6	8.8, 10.6	8.6, 10.8, 12.6, 13.8	9.0, 11.4, 14.4
	bending	10.4, 12.2, 14.4, 17.6	8.6, 10.8, 14.4	8.4, 10.6, 14.6, 16.2, 16.8, 17.6	8.6, 10.8, 12.2, 14.4

4. Conclusion

In summary, we have successfully simulated the local atomic structure and phonon LSDOS for the cubic Gd_2O_3 crystal with trivalent Eu impurities occupying S_6 crystallographic sites. The calculations were carried out within a shell model, the reliability of which is confirmed by the good agreement between the calculated and measured data for some physical quantities of perfect Gd_2O_3.

The simulation predicts an increase in the distances between Eu ion and nearest ions as compared to bond lengths in the perfect crystal. The lattice dynamics calculations allowed to determine the frequencies of Eu impurity-induced vibrations in Gd_2O_3:Eu.

Acknowledgments

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